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(21) International Application Number: PCT/DK95/00428 (22) International Filing Date: 27 October 1995 (27.10.95) (30) Priority Data: 1257/94 28 October 1994 (28.10.94) DK (71) Applicant (for all designated States except US): NOVO NORDISK A/S [DK/DK]; Nova Allé, DK-2880 Bagsværd (DK). (72) Inventors; and (75) Inventors/Applicants (for US only): LUND, Henrik [DK/DK]; Novo Nordisk A/S, Novo Allé, DK-2880 Bagsværd (DK). KIRK, Ole [DK/DK]; Novo Nordisk A/S, Novo Allé, DK-2880 Bagsværd (DK). MUNK, Niels [DK/DK]; Novo Nordisk A/S, Novo Allé, DK-2880 Bagsværd (DK). (74) Common Representative: NOVO NORDISK A/S; Corporate Patents, Novo Allé, DK-2880 Bagsværd (DK).	(81) Designated States: AL, AM, AT, AU, BB, BG, BR, BY, CA, CH, CN, CZ, DE, DK, EE, ES, FI, GB, GE, HU, IS, JP, KE, KG, KP, KR, KZ, LK, LR, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, TJ, TM, TT, UA, UG, US, UZ, VN, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG), ARIPO patent (KE, LS, MW, SD, SZ, UG). Published <i>With international search report.</i> <i>Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i>	

(54) Title: **A PROCESS FOR CHEMICAL FINISHING OF INSOLUBLE POLYMERS**

(57) Abstract

A process for enzymatically catalyzing an esterification of insoluble polymer fibres containing free hydroxy groups by reacting the polymer fibres with a carboxylic acid such as a carboxylic acid having the general formula $R-COOR^1$, wherein R is linear or branched C_{1-25} alkyl, preferably linear C_{3-25} alkyl, more preferably linear C_{8-25} alkyl, which optionally is substituted with one or more carboxy, nitro, chloro, bromo, fluoro, amino, hydroxy, keto; and R^1 is hydrogen, C_{1-4} alkyl, or vinyl, preferably methyl, ethyl or vinyl; or an ester thereof, preferably an enolester, in the presence of an enzyme capable of catalyzing esterification, especially a lipase or an esterase, is useful for chemical finishing of yarn, textile, fabric, papermaking pulp, cardboard or paper, the fibre or fabric made therefrom having improved functional properties such as reduced tendency to wrinkling, improved durable softness, anti-static appearance, water repellency, enhanced soil release or flame retardancy.

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A PROCESS FOR CHEMICAL FINISHING OF INSOLUBLE POLYMERS

The present invention relates to a process for chemical
5 finishing of insoluble polymers. More specifically, the
invention relates to an enzymatic esterification of insoluble polymers wherein organic molecules containing a
carboxylic acid residue are covalently linked to insoluble polymers such as cellulosic fibres or textile fabric,
10 the fibre or fabric made therefrom having improved functional properties such as reduced tendency to wrinkling, improved durable softness, anti-static appearance, water repellency, enhanced soil release or flame retardancy.

15

BACKGROUND OF THE INVENTION

In chemical finishing of textile fabrics two traditional
20 ways of processing have been to either deposit a chemical compound or composition onto the fabric or to chemically reacting, e.g. cross-linking, certain useful compounds with the fabric.

25 Examples of deposit compounds are the application of softener finishes which may improve the hand and drape of fabrics, add body to the fabric, facilitate application of other finishes and increase the life and utility of the fabric. Softeners are usually available in three types:
30 nonionic, anionic and cationic. As groups the anionic and nonionic softeners usually serve more as lubricants rather than softeners, while the cationic softeners are probably the best softening agents available. The cationic softeners impart a soft, silky and bulky hand in
35 the fabric. The most common type of cationic softeners are the quaternary ammonium salts which have affinity for

most textile fibers, as due to their positive charge. Since most fibers develop a negative surface charge in water, the cationic softeners exhaust onto the fibers.

- 5 In recent years there has, however, been an increasing environmental concern about the usage of the quaternary ammonium salts as due to their poor bio-degradability as well as their fairly high toxicity.
- 10 Among reacting finishes for fabric, DMDHEU (Di-Methylol-Di-Hydroxy-Ethylene-Urea) is the most widely used for durable press treatment. At high temperature with presence of an acid catalyst it reacts with free hydroxy groups and creates internal crosslinks in the fibres. Release of
- 15 residual formaldehyde compounds is a major concern, due to the toxicity of these compounds. An alternative formaldehyde free durable press treatment uses esterification with BTCA (1,2,3,4-Butane-Tetra-Carboxylic-Acid) at elevated temperatures in acid or with presence of a cata-
- 20 lysts. The acid process causes damage to the fabric, whereas the catalysts e.g. hypophosphites have given reason to environmental concerns. These formaldehyde free treatments therefore have had limited application.
- 25 In order to obtain desirable end properties, paper or cardboard materials are conventionally finished with a synthetic coating such as oxidized polyethylenes, ethylene-acrylic acid, ketone resin, ureaformaldehyde, melamine formaldehyde, anionic latex etc. Due to environmental
- 30 concerns, it is desirable to replace the petrochemically based coatings, with coatings based on renewable resources, in order to make entirely CO₂-neutral paper and cardboard materials.
- 35 Carboxylic ester hydrolases (EC 3.1.1), especially lipa-

ses and esterases, are well known as catalysts capable of catalyzing synthesis of esters by reacting an alcohol with either a carboxylic acid or an ester thereof solubilized in an organic solvent with low water-activity.

5 Furthermore, these catalysts have proven efficient for esterification of various carbohydrates solubilized in organic solvents. Even though suspension of free enzymes have shown some effect immobilized enzymes have preferably been used as they exhibit improved stability in
10 the organic solvents and, furthermore, offer obvious benefits regarding re-use of the catalyst. One example is the esterification of simple alkyl glucosides catalyzed by immobilized lipases in organic solvents with low water activity described in US 5,191,071.

15

Recently, various methods have been developed for solubilizing enzyme catalysts in organic media by either chemical modification of the enzyme with organic polymers such as polyethyleneglycol (PEG) (K. Takahashi et al. Biochem.

20 Biophys. Re. Commun. 1984, 121, 261 and T. Yoshimoto et al. Biotech Lett. 1984, 6, 337 and K. Takahashi et al. J. Org. Chem. 1985, 50, 3414) or by complexing the catalyst with organic polymers (Y. Okahata and K. Ijiro, Bull. Chem. Jpn, 1992, 65, 2411). These methods have enabled

25 reaction between solubilized organic substrates and soluble enzyme catalysts.

As described above, both immobilized and solubilized enzymes have been shown to be efficient for catalyzing
30 esterification reactions by combining various solubilized substrates (including simple carbohydrates) in a suitable organic solvent with low water activity. However, no esterification of insoluble substrates has, so far, been described in the prior art.

35

SUMMARY OF THE INVENTION

Surprisingly, it has been found that hydrolytic enzymes such as carboxylic ester hydrolases (EC 3.1.1),
5 preferably lipases or esterases, are capable of catalyzing esterification of insoluble polymer substrates, preferably polymers such as cellulose and lignocellulose.

Based on this finding it is now possible to carry out
10 chemical finishing of textile, fabric, yarn etc. containing insoluble polymer fibres, especially cellulosic or lignocellulosic fibres, by an enzymatic process in which a hydrolytic enzyme such as a lipase or an esterase catalyzes the formation of ester bonds between the polymer
15 and a suitable reactant, i.e. an acyldonor preferably containing one or more carboxy functions.

Accordingly, the present invention provides a process for enzymatically catalyzing an esterification of insoluble
20 polymer fibres containing free hydroxy groups, wherein the polymer fibre is reacted with a carboxylic acid or an ester thereof in the presence of an enzyme capable of catalyzing esterification.

25 An advantage of the enzymatic esterification according to the invention is that the surfaces of porous materials can be modified selectively, since access to the interior of the material is restricted for the large enzyme molecules. Unlike many conventional processes, it may thus be
30 possible to retain the basic structure of e.g. cellulosic fibres which have inherent strength and good chemical resistance properties. Further, it is contemplated that surface esterification of fabric can be used to prepare hitherto unknown fabric types with improved functional
35 properties. For example, it is contemplated that lipase catalyzed ester formation with fatty acids is useful for

providing permanent wash-resistant water-repellancy to cotton or water-repellancy to cardboard boxes or containers, based on renewable materials.

5 Chemical finishing of textiles, fibres and yarns serves to improve the properties of the resulting product, usually a textile e.g. for garments, carpeting, upholstery. Examples of such properties are permanent press, softening, soil release, water repellancy and flame retardancy. The present invention provides a process by which, in
10 dependance of the chemical compound actually attached to the polymer fibre by an ester bond, one or more of the desired properties may be obtained or improved in an easy, economical and environmentally friendly way.

15

Further, the process of the invention provides a durable finishing of the polymer fibre, i.e. provides a permanent improvement to the polymer fibre, which is in contrast to deposition finishings wherein a chemical compound is de-
20 posited on the polymer and, thus, may be easily removed mechanically when laundering or wearing or otherwise using the polymeric, preferably cellulosic or lignocellulosic, material.

25 In another aspect, the process of the invention relates to finishing of any insoluble polymeric material possessing free hydroxy groups, i.e. insoluble polymeric material present in other forms than as a fibre.

30

DETAILED DESCRIPTION OF THE INVENTION

The polymeric substrate

35 In the present specification and claims, the term "insoluble polymer fibre containing free hydroxy groups" is

intended to mean a polymeric fibrous material having hydroxy groups capable of forming ester bonds when contacted with carboxy groups, i.e. carboxylic acids or esters thereof.

5

Preferably, the polymeric fibrous material subjected to the process of the invention is present as a fiber, a staple fiber such as a solvent-spun fiber, a filament, a thread, a yarn, or a textile fabric which may be woven,
10 nonwoven or knitted.

In a preferred embodiment of the invention, the polymer fibre is a cellulosic polymer fibre, i.e. containing cellulose or cellulose derivatives, preferably prepared from
15 cotton, viscose (rayon), lyocell, flax (linen), ramie, or any blend thereof; and blends thereof with polyesters, wool, polyamides and (poly)acrylics. Typical examples of such blends are viscose/cotton, viscose/polyester, lyocell/polyester, lyocell/cotton, cotton/acrylic, cotton/polyester, cotton/polyester/acrylic,
20 cotton/polyamide/polyester.

In another preferred embodiment of the invention the polymer is a lignocellulosic fibre, for example paper or
25 cardboard made from chemical or mechanical pulps of plant or wood fibres.

In yet another preferred embodiment of the invention, the polymer is synthetic polymer. Preferably, the synthetic
30 polymer is selected from the group consisting of polyesters, polyamides, nylons, (poly)acrylics and co-polymers thereof.

Th carb xylic acid est r

In the present specification and claims, the term "carboxylic acid or an ester thereof" is intended to mean any
5 carboxylic acid or ester which improves one or more properties of the polymeric material and is capable of forming ester bonds with the free hydroxy groups of the polymer.

10 It is contemplated that, e.g. for obtaining an improvement of the softening finish, i.e. improvement of the hand and drape of the final fabric, for obtaining flame retardancy, for obtaining water repellancy and for obtaining resin finishing ("permanent press"), it may be convenient to use in the process of this invention a carboxylic acid or an ester thereof with the general formula
15 (I)



20

wherein

R is linear or branched C_{1-25} alkyl, preferably linear C_{3-25} alkyl, more preferably linear C_{4-25} alkyl, which optionally is substituted with one or more carboxy, nitro, chloro,
25 bromo, fluoro, amino, hydroxy, keto; and
R¹ is hydrogen, C_{1-4} alkyl, or vinyl, preferably methyl, ethyl or vinyl.

For obtaining permanent press, it is advantageous to use
30 a poly-carboxylic acid or an ester thereof, i.e. a carboxylic acid with two or more carboxy groups capable of forming ester bonds.

For obtaining flame retardancy, it is advantageous to use
35 a halogen-substituted carboxylic acid or an ester thereof, i.e. a fluorinated, chlorinated or bromated carboxy-

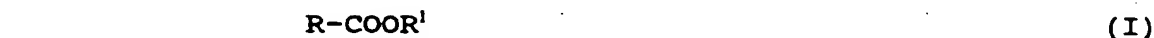
lic acid or an ester thereof.

Further, it is contemplated that the process of the invention is useful for dyeing, preferably for dyeing with
5 a reactive textile dyestuff, the polymeric fibre or material by reacting the polymeric fibre or material with a carboxylic acid or ester thereof of the general formula (I)



wherein R comprises a chromophore and R¹ has the meaning set forth above. Usually, the chromophore comprises one or more heterocycles, preferably comprising one or more
15 nitrogen, sulphur or oxygen atoms. Examples of useful chromophores are derivatives of acridines and phenazines.

Further, it is contemplated that the process of the invention is useful for obtaining brightness, e.g. optical
20 brightness, of the polymeric material by reacting the polymeric material with an carboxylic acid or ester thereof of the general formula (I)



wherein R comprises a fluorophore and R¹ has the meaning set forth above. Examples of useful fluorophores are derivatives of xanthenes.

30 Further, it is contemplated that the process of the invention is useful for obtaining water repellancy of the polymeric material by reacting the polymeric material with a wax or a derivative of a wax containing one or more carboxy groups capable of forming ester bonds.

35 Other carboxylic acid esters which may advantageously be

used in the process of the present invention are enol -
sters. By using enolesters in the process, the chemical
reaction process is irreversible and results in a ketone
or aldehyde reaction side product.

5

The enzyme

In the present specification and claims, the terms "lipa-
se" and "esterase" are intended to mean carboxylic ester
10 hydrolases (EC 3.1.1), especially an enzyme that in an
aqueous environment hydrolyses ester linkages present in
either water-soluble molecules or water in-soluble mole-
cules (e.g. long chain lipids).

15 Enzymes suitable for the process of the present invention
can be selected by the following method, utilizing the
reversible nature of the esterification reaction, impli-
cating that an enzyme able to catalyze ester formation
will also be able to catalyze the hydrolysis of ester-
20 bonds.

Cellulose esters are prepared according to the acid-
chloride pyridine procedure of C.J. Malm et.al, (Ind. and
Eng. Chem, Vol. 43, No.3, march 1951). The cellulose
25 esters are incubated with the enzyme preparation in an
agar gel containing phenol-red. 1000 ml agar gel is pre-
pared from 17 g Agarose type 2 medium EEO, Sigma, A-6877,
3 gram NaNO_3 , 1 gram K_2HPO_4 , 0.5 gram KCl , 1 ml 1% FeSO_4 ,
and 50 ml 0.4 gram/litre phenol-red solution.

30

If the enzyme hydrolyses the ester, carboxylic acid is
liberated and will diffuse into the gel, changing the
color from red to yellow. A number of controls must be
run to avoid false positive or negative results: Ester
35 without enzyme and enzyme without ester must both turn
out negative in the test, and enzyme with glycerine tri-

butyrate should react positively and give colour change.

The lipase is suitably a microbial or an animal-derived lipase. As such, the parent lipase may be selected from yeast, e.g. Candida lipases, bacterial, e.g. Pseudomonas lipases or fungal, e.g. Humicola or Rhizomucor lipases. More specifically, suitable lipases may be the Rhizomucor miehei lipase (e.g. prepared as described in EP 238 023), Humicola lanuginosa lipase e.g. prepared as described in EP 305 216 (available from Novo Nordisk under the trade name Lipolase™), Candida antarctica lipase A or B, or Pseudomonas cepacia lipase. Other examples of suitable lipases are variants of any one of the lipases mentioned above, e.g. as described in WO 92/05249 or WO 93/11254. Examples of animal-derived lipases are lipases extracted or otherwise derived from porcine pancreas or from guinea-pigs.

A useful esterase is suitably one of microbial origin. As such the esterase may be either fungal, bacterial or from yeast.

Other useful enzymes are chemically modified lipases or esterases which may be obtained by the coupling of a polyethyleneglycol (PEG) to amino acid residues in the lipase as described in K. Takahashi et al. 1984, T. Yoshimoto et al., and K. Takahashi et al. 1985; or by complexing the lipase with organic polymers as described in Y. Okahata and K. Ijiri.

Other useful enzymes are lipases or esterases which are modified as described in WO 95/09909, i.e. glucosaminated enzymes having a higher pI than the unmodified (parent) enzyme.

Definition of Lipase Units (LU)

The lipase activity is determined in the following assay:
A substrate for lipase is prepared by emulsifying glycerine tributyrat (MERCK) using gum-arabic as emulsifier.
5 Lipase activity is assayed at pH 7 using pH stat method.
One unit of lipase activity (LU) is defined as the amount of enzyme needed to liberate one micromole ($1 \mu\text{M}$) fatty acid per minute.

10 Process conditions

It is obvious to the skilled person that the process must be carried out under conditions (e.g. temperature, pH, solvent) which favours the esterification process over
15 the undesired hydrolytic cleavage of ester bonds. Accordingly, it is impossible to carry out the desired esterification process when using water as a solvent.

The process of the invention may be carried out in a suitable solvent. Preferably, the solvent is a water-immiscible organic solvent. It is contemplated that conventional organic solvents except alcohols are useful in the process of the invention. Examples of useful solvents are iso-octane, n-hexane and cyclohexane.
20

25 However, when the carboxylic acid or the ester to be used is liquid at the process temperature, the process may be carried out without a solvent.

30 Alternatively, the reaction may take place in a microemulsion formed by adding a carboxylic acid or an ester thereof to a mixture of water and a suitable surfactant. Typically, the surfactant is a nonionic surfactant.

35 The following non-limiting example illustrates the invention.

EXAMPLE 1

A cotton swatch (2 x 2 cm) was added to a solution of decanoic acid (50 mg) in butanone (10 ml). Lipase A from *Candida antarctica* (5 LU/mg, available from Novo Nordisk A/S) was then added and the mixture was vigorously stirred at 50°C for 24 hours. The swatch was then rinsed thoroughly in butanone (3 x 10 ml) and dried at room temperature for 2 hours. The swatch was then treated with an aqueous solution (5 ml) of sodium hydroxide (1 M) at 40°C for 1 hour. The swatch was removed and the solution was then acidified with hydrochloric acid to a pH of 2. Extraction of this solution with chloroform (5 ml) afforded an extract which was evaporated in vacuo. Analysis by NMR spectroscopy (employing a Bruker acp 300 NMR spectrometer and using deuterated chloroform as solvent) indicated the extract to contain decanoic acid.

Another swatch was treated as above, only adding no enzyme to the butanone. NMR analysis failed to prove any presence of decanoic acid in the final chloroform extract.

Accordingly, this example shows that the first swatch had been successfully esterified with decanoic acid in the presence of Lipase A as the catalyst.

EXAMPLE 2

30

Lipase-catalyzed surface modification of cotton

For preparation of a butyrate (C4) esterified fabric, an 8x8 cm swatch of pure cotton knit was dried, and immersed in a solution of 1 g vinyl-butyrate dissolved in 160 ml iso-octane. 200 micro litre of lipase derived from PEG

modified *Candida antarctica* Lipase A (5 LU/mg) was mixed into the solution, and the solution with the swatch was incubated 4 hours at 60°C under gentle stirring. The swatch was removed, dried, washed with demineralized water and dried again.

Another swatch was surface derivatized into a laurate (C12) ester by similar treatment, but in stead of 1 g vinyl-butyrate, 1.5 g vinyl-laurate was used. After incubation this swatch was washed with methanol, before washing with demineralized water and drying.

A third swatch was used as reference

The formation of the ester bonds was verified with photoacoustic Fourier transformed infrared spectroscopy, showing carbonyl ester peaks near 1740 cm⁻¹, except for the reference swatch.

20 Test of water-absorptive properties

The water absorptive properties of the modified cotton swatches was tested with a Tensiometer (Sigma 70, KSV, Finland). With a constant rate of 20 mm/second this apparatus cyclically dips the swatch 2mm into water and elevates it to 5 mm above the water surface. It then dips the swatch again, and repeats the cycle. The weight of the swatches between each dip is recorded. The results are shown in table 1.

TABLE 1

Water uptake g/g	Reference	C-4 cellulose ester	C12 cellulose ester
0 dips	0	0	0
2 dips	0.8	2.6	0.3
4 dips	1.3	2.7	0.7
6 dips	1.6	2.7	0.9
8 dips	1.9	2.7	1.1
10 dips	2.0	2.7	1.2
12 dips	2.3	2.7	1.3

The results show that the surface treatments have caused major changes in the properties of the cotton knit. The C-4 esterified cotton takes up water at a higher rate than the reference, whereas the C-12 esterified cotton has reduced the water-uptake two-fold.

A drop test was also carried out: Droplets of 10 μ -litre demineralized water was placed on the surface of each swatch. The time elapsed when the droplets had disappeared was recorded. Results from three repeated experiments are given in table 2.

TABLE 2

	seconds	seconds	seconds
Reference	20	20	20
C-4 esterified	1	1	2
C-12 esterified	>3600	>3600	>3600

The results show that the C4-esterified cotton has much enhanced water suction performance compared to the reference, and thus is particularly suited for use in e.g. towels. The C-12 esterified cotton has become completely
5 repellent to water droplets, and thus could be particularly useful in e.g. out-door wear.

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121, 261

5

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1951

15

CLAIMS

1. A process for enzymatically catalyzing an esterification of insoluble polymer fibres containing free hydroxy groups, wherein the polymer fibres are reacted with a carboxylic acid or an ester thereof in the presence of an enzyme capable of catalyzing esterification.
2. The process according to claim 1, wherein the polymer fibres are present as yarn, textile, fabric, papermaking pulp, cardboard or paper.
3. The process according to claim 1 or 2, wherein the polymer is a cellulosic polymer, preferably a cellulosic polymer selected from the group consisting of cotton, viscose (rayon), lyocell, flax (linen), ramie, and any blend thereof; and blends thereof with polyesters, wool, polyamides and (poly)acrylics.
4. The process according to claim 1 or 2, wherein the polymer is a synthetic polymer, preferably a synthetic polymer selected from the group consisting of polyesters, polyamides, nylons and (poly)acrylics.
5. The process according to claim 1 or 2, wherein the polymer fibres are lignocellulosic polymer fibres, preferably lignocellulosic polymer fibres obtained from wood or plants, more preferably paper or cardboard made from chemical or mechanical pulps of plant or wood fibres.
6. The process according to any of the claims 1-5, wherein the carboxylic acid or the ester thereof has the general formula (I)

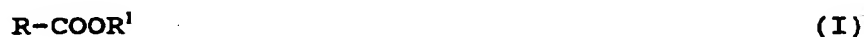


(I)

wherein

R is linear or branched C₁₋₂₅ alkyl, preferably linear C₃₋₂₅ alkyl, more preferably linear C₈₋₂₅ alkyl, which optionally is substituted with one or more carboxy, nitro, chloro, bromo, fluoro, amino, hydroxy, keto; and
R¹ is hydrogen, C₁₋₄ alkyl, or vinyl, preferably methyl, ethyl or vinyl.

7. The process according to any of the claims 1-5, wherein the carboxylic acid or the ester thereof has the general formula (I)



wherein R comprises a chromophore or a fluorophore.

8. The process according to any of the claims 1-6, wherein the carboxylic acid or the ester thereof is a wax or is derived from a wax.

20

9. The process according to any of the claims 1-6, wherein the carboxylic acid ester is an enolester, preferably vinylester or isopropenylester.

25 10. The process according to any of the claims 1-9, wherein the enzyme is a lipase, preferably a microbial lipase, which optionally is chemically modified.

11. The process according to any of the claims 1-9, wherein the enzyme is an esterase.

30

INTERNATIONAL SEARCH REPORT

International application No.

PCT/DK 95/00428

A. CLASSIFICATION OF SUBJECT MATTER

IPC6: D06M 16/00, D06M 13/184

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC6: D06M

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

SE,DK,FI,NO classes as above

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

WPI, CA, CLAIMS

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 5191071 A (OLE KIRK ET AL), 2 March 1993 (02.03.93)	1-11
A	US 5042986 A (JOHN D. KITCHENS ET AL), 27 August 1991 (27.08.91)	1-11
A	DE 4012351 A1 (VEDA, SOFIA/SOFIJA, BG), 24 October 1991 (24.10.91)	1-11

☐ Further documents are listed in the continuation of Box C.
 ☒ See patent family annex.

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Date of the actual completion of the international search

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INTERNATIONAL SEARCH REPORT
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Patent document cited in search report	Publication date	Patent family member(s)	Publication date
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		WO-A- 8901480	23/02/89
US-A- 5042986	27/08/91	NONE	
DE-A1- 4012351	24/10/91	FR-A- 2661420	31/10/91